Influence of Exchangeable Cations on Water Adsorption by Soil Clays

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ABSTRACT

The interaction of water with the clay fractions (<2 μm) from two midwestern soils was studied using Fourier transform infrared (FTIR) spectroscopy and gravimetric methods. The soil clay fractions were obtained from a Blount loam (fine, illitic, mesic Aeric Epiaqualfs) and a Fayette silty clay loam (fine-silty, mixed, mesic, superactive Typic Hapludalfs). These clay fractions were exchanged with Mg^{2+}, 50:50 Ca^{2+}/Mg^{2+}, Ca^{2+}, Na^+, and K^+ to determine the influence of the exchangeable cation on their water sorption behavior. Water sorption isotherms and FTIR spectra of the clays were collected simultaneously using a gravimetric-spectroscopic cell. Overall, the amount of water sorbed by the samples increased as the ionic potential of the exchangeable cation increased and was strongly correlated to the hydration energy of the cations ($P > F < 0.0001$). The position of the H–O–H bending band (ν_2 mode) also increased with increasing ionic potential of the exchangeable cation indicating strengthening of water H bonds. In addition, it was observed that the position of this band decreased with increasing water content for the Mg-exchanged clays compared with an overall increase for the Ca-exchanged samples. X-ray diffraction patterns indicated an expansion of the phyllosilicate clay minerals as the water activity increased; however, no differences were observed between the Ca- and Mg-exchanged samples. This study shows that the molecular properties of water on Ca- and Mg-exchanged soil clays are similar to that on specimen clays and provides new insight about the role of exchangeable cations in soils.

THE INTERACTION OF WATER with soil colloids plays a critical role in all areas of soil science, and numerous studies have shown that exchangeable cations significantly influence soil–water relations. Dispersion and clay swelling, which are enhanced by Na and Mg on the soil exchange complex (Rengasamy, 1983; Rengasamy et al., 1986; Shainberg et al., 1988; Heil and Sposito, 1993; Curtin et al., 1994; Dontsova and Norton, 2002), can block air- and water-conducting soil pores, thereby affecting infiltration (Keren, 1989, 1990, 1991; Dontsova and Norton, 2002) and hydraulic conductivity (Bakker and Emerson, 1973; Alperovitch et al., 1981; Levy et al., 1988; Curtin et al., 1994; Zhang and Norton, 2002). By contrast, Ca is known to promote the flocculation of soil colloids (Rengasamy, 1983; Rengasamy et al., 1986; Heil and Sposito, 1993; Curtin et al., 1994; Dontsova and Norton, 2002) and is often used in various soil remediation strategies. Although exchangeable cations are known to affect the overall behavior of water in soils, relatively

little is known about the molecular mechanisms of soil–water interactions underlying this behavior. A considerable amount of work has been conducted on specimen clay minerals and their interaction with water, but it is not clear if similar mechanisms are operative in soils. There is some recent work showing that soils clays behave differently than specimen clays because the solid phases are more complex and include organic matter (OM) (Zachara et al., 1993).

The interaction of water with expandable clay minerals has been an active area of research for more than 60 yr (Buswell et al., 1937; Mooney et al., 1952b; Keren and Shainberg, 1975, 1979; Poinsignon et al., 1978; Hall and Astill, 1989; Johnston et al., 1992; Berend et al., 1995; Cases et al., 1997; Chiou and Rutherford, 1997; Dios Cancela et al., 1997; Xu et al., 2000; Madejova et al., 2002). Water condensation and osmotic swelling are the dominant mechanisms for retaining water molecules at high relative humidity (RH). At low water contents, the hydration characteristics of smectite depend strongly on the exchangeable cation (Berend et al., 1995; Cases et al., 1997; Dios Cancela et al., 1997; Xu et al., 2000). Layer charge also affects the amount of water adsorbed on clay surfaces, with more water being adsorbed on high charged smectites than on low charged ones (Chiou and Rutherford, 1997; Laird, 1999; Xu et al., 2000). However, Laird (1999) showed that effective hydration numbers of exchangeable cations decrease with increase in layer charge.

Water sorption by expandable clay minerals is generally accompanied by an increase in basal spacing or swelling caused by hydration of the interlayer cations and the exposed clay surfaces at low water contents, followed by osmotic effects when free water is present (Keren and Shainberg, 1975; Sposito and Prost, 1982). Berend et al. (1995) and Cases et al. (1997) observed an increase in basal spacing with the hydration energy of the saturating cation: $Cs^+ < Rb^+ < K^+ < Na^+ < Li^+ < Ba^{2+} < Sr^{2+} < Ca^{2+} < Mg^{2+}$. For Mg- and Ca-smectite, a homogeneous two-layer hydrate predominated over a wide range of RH, and a two-layer hydrate was formed for all divalent cations at high RH. Farmer (1978) reviewed several studies of the swelling of clays exchanged with different cations, and observed a trend for increased swelling at high RH with an increase in cation hydration energy. Differences in clay basal spacings among different divalent cations, though, were small and inconsistent. Greater differences between the d-spacings of Ca and Mg exchanged clays were observed

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Abbreviations: BET, Brunauer-Emmett-Teller; CEC, cation exchange capacity; EGME, ethylene glycol monoethyl ether; EIRM, Environmental Infrared Microbalance; FTIR, Fourier transform infrared; IR, infrared; I/S, randomly interstratified illite-smectite; OM, organic matter; P/P_0, partial pressure of water vapor; RH, relative humidity.

in suspensions, where osmotic forces were dominant (MacEwan and Wilson, 1980; Slade and Quirk, 1991).

The properties and local environment of adsorbed water on clay surfaces can be assessed using infrared (IR) spectroscopy because the vibrational modes of water are highly sensitive to changes in their local environment. Specifically, the ν(OH) bands of water at 3580 and 3420 cm^{-1} decrease in position with a concomitant increase in position of the δ(HOH) band at 1635 cm^{-1} with increased H bonding (Pimentel and McClellan, 1960). A number of researchers have observed a shift in the position of the stretching (Poinsignon et al., 1978; Prost [1975] as quoted in Sposito and Prost, 1982; Xu et al., 2000; Madejova et al., 2002) and bending (Johnston et al., 1992; Yan et al., 1996; Xu et al., 2000; Madejova et al., 2002) bands of water sorbed to smectites. Generally, as the water content of the clay decreased, the position of the stretching vibration shifted to a higher frequency, while the position of the bending vibration shifted to a lower frequency, indicating a decrease in H bonding. It has also been reported that the position of the water stretching band decreased and the deformation band increased with an increase in ionic potential of the exchangeable cation (Prost [1975] as quoted in Poinsignon et al., 1978; Madejova et al., 2002).

Johnston et al. (1992) and Xu et al. (2000) used an environmental infrared microbalance (EIRM) to study water sorption by smectites. The apparatus combined an FTIR spectrometer and a microbalance in a controlled environment chamber. This arrangement allowed simultaneous collection of the infrared spectra and weight of the sample in situ, providing a method to correlate macroscopic sorption characteristics with molecular vibrational data (Johnston et al., 1992; Tipton et al., 1993). It also permitted the dry mass of the sample to be obtained without complete desiccation (Xu et al., 2000), which can change the water sorption properties of clay minerals (Hall and Astill, 1989).

The objective of this investigation was to evaluate the effects of exchangeable cations and clay mineralogy on water sorption by soil clays using the EIRM technique and water as a vibrational probe. Because of their importance in soils, we specifically investigate the nature of water in contact with clays exchanged with Na, K, Mg, Ca, and a mixed Ca/Mg exchanged phase. Although considerable mechanistic information is available for water sorption on specimen clay minerals, very little is known about the molecular-level interaction of water with soil clays related to either the nature of the exchangeable cation or the mineralogy of the soil. We hypothesize that relationships previously observed for specimen smectites can largely be extended to soil clays.

MATERIALS AND METHODS

Soil Clay Samples

Clay fractions (<2 μm) from the surface horizons (0–20 cm) of two agricultural soils previously studied by Dontsova and Norton (2002) were used in this study. These included a Blount soil from Williams County, OH, and a Fayette soil from Clinton County, IA. Whole soil properties are discussed in Dontsova and Norton (2002) and are summarized in Table 1.

The soil clay fractions were separated by repeated suspension and sedimentation in deionized water using an automatic fractionator (Norton, unpublished data, 1983). Separation was essentially complete for the Blount soil, but the procedure extracted only about half the available clay from the Fayette soil because OM was not destroyed and served as a strong aggregating agent. Subsamples of the freeze-dried clays were repeatedly washed with 0.5 M solutions of CaCl$_2$ and MgCl$_2$, and 1 M solutions of KCl and NaCl and then washed free of Cl$^-$ by centrifugation with water. Clays with approximately 50:50 exchangeable Ca/Mg were prepared from solutions of CaCl$_2$ and MgCl$_2$ mixed in proportions that accounted for the preferential exchange of Ca (35:65 and 40:60 for Blount and Fayette samples, respectively) (Dontsova and Norton, 2001). Approximately 15 mg mL^{-1} clay suspensions were obtained for FTIR studies.

FTIR–Gravimetric Studies

A 0.45-mL aliquot of each clay suspension was sedimented onto a polypropylene film in a wire loop of 18 mm diam. and allowed to dry overnight under ambient conditions. The wire loop proved to be an effective means of obtaining self-supporting films of otherwise unstable samples (Dontsova, 2002). Fourier transform infrared spectra and gravimetric data were obtained simultaneously with the EIRM used in earlier water sorption studies (Johnston et al., 1992; Xu et al., 2000). The self-supporting clay film contained in the wire loop was suspended from a Cahn D-2000 microbalance inside a controlled environment cell. The partial pressure of water vapor (P/P$_0$) in the cell was decreased from 1 to 0 and then raised to 1. The P/P$_0$ was changed at 0.05 increments from a P/P$_0$ of 0 to 0.5 and at 0.1 increments from 0.5 to 1. At each P/P$_0$ step, the sample was equilibrated for 2 h. The partial pressure of water vapor was changed by mixing streams of dry N$_2$ gas and N$_2$ gas saturated with water vapor (total flow was 100 std cm^3 min^{-1}); and monitored using a Vaisala model HMP35A humidity probe (Vaisala Oyj, Helsinki, Finland). The experiment was controlled by the LabView program, version 5.1 (National Instruments Corporation, Austin, TX). Fourier transform infrared spectra (PerkinElmer 1600 spectrometer with a DTGS detector and a KBr beamsplitter, PerkinElmer, Inc., Welles-

Table 1. Selected mineralogical, physical, and chemical properties of the soils and their clay fractions (CF).

Soil	Dominant clay minerals†	CEC‡		Clay	OM		EGME SA	
		Soil	CF		Soil	CF	Soil	CF
		— cmol$_c$ kg^{-1} —			— g kg^{-1} —		— m^2 g^{-1} —	
Blount L	I(3), K(2), HIV(2)	21.7	28.2	254	24	43	70	156
Fayette SiCL	I/S(4), K(3), I(3), V(2)	22.7	38.9	291	14	27	93	255

† HIV = hydroxy-interlayered vermiculite; I = illite; I/S = randomly interstratified illite-smectite; K = kaolinite; V = vermiculite; (1) through (5) = relative abundance with (1) = least abundant and (5) = most abundant.
‡ CEC = cation exchange capacity by summation of natural exchangeable cations for whole soil and by exchange of Mg for Ca in CF; OM = organic matter; EGME SA = surface area by ethylene glycol monoethyl ether method, soil ground to <0.25 mm, CF exchanged with Mg.

ley, MA) were obtained every hour, whereas gravimetric and RH measurements were taken every minute. The unapodized resolution of the FTIR spectra was 4 cm^{-1} with a step interval of 2 cm^{-1}. Spectra were analyzed using the GRAMS/32 software, version 5.2 (Thermo Electron Corp., Waltham, MA). The position and absorbance of the H–O–H deformation vibration was determined by curve-fitting a Gaussian-Lorentzian lineshape to the spectrum in the 1800 to 1510 cm^{-1} region after baseline correction.

The experimental design was a randomized block with cation as the treatment. At least two replications were done for each treatment. The SAS ANOVA (SAS Institute, 1990) procedure was used to find significant differences between treatments within clays at the 95% level. Comparisons of treatments across clays were performed using a simple t test.

The Brunauer-Emmett-Teller (BET) equation was applied to the water adsorption data to determine monolayer coverage, x_m, and the surface area, S_m, of the clays exchanged with different cations. Using the BET equation, it was possible to relate the mass of adsorbate per unit mass of sample, q, to the RH or partial pressure of water vapor, P/P$_0$:

$$\frac{P/P_0}{q(1 - P/P_0)} = \frac{1}{x_m C} + \frac{(C - 1)}{x_m C}\left(\frac{P}{P_0}\right) \qquad [1]$$

where C, a constant that characterizes the affinity of the adsorbate for the surface, is a function of the difference between adsorbate's enthalpies of desorption and vaporization (Atkins, 1998, p. 861):

The surface area was calculated from Sposito (1984):

$$S_m = (x_m/M_r)N_A a_m \times 10^{-15} \qquad [2]$$

where x_m is kilograms of adsorbate per kilogram of sample at monolayer coverage, M_r is the relative molecular mass of the adsorbate (18 g mol^{-1} for water), and a_m is its packing area in square nanometers (0.106 nm^2 for water) (Sposito, 1984). For comparison, surface areas were also measured on Mg-clays using the simplified ethylene glycol monoethyl ether (EGME) method (Cihacek and Bremner, 1979).

X-ray Diffraction Study

Layer spacing (d$_{001}$) of the soil clays at different RHs was determined from oriented mounts prepared by sedimentation of Mg- and Ca-exchanged clay onto 27 by 46 mm glass slides. Samples were placed inside a chamber with controlled RH, which was mounted onto the diffractometer. Constant partial pressure of water vapor was maintained around the sample by continuous flow of a mixture of dry N$_2$ gas and N$_2$ gas saturated with water vapor in the following proportions: 1:0, 0.8:0.2, 0.6:0.4, 0.4:0.6, 0.2:0.8, and 0:1. Water vapor P/P$_0$ in the chamber was monitored with a RH probe, and samples were equilibrated at each P/P$_0$ step for 2 h (Cases et al., 1997).

X-ray diffraction patterns were obtained using CuKα-radiation generated at 30 kV and 28 mA, incident and diffracted beam Soller slits, a Kevex PSi Si (Li) detector and a Siemens D-500 θ–θ diffractometer. The samples were step-scanned from 2 to 30° 2θ at 0.05° 2θ increments with a counting time of 2 s per increment. The position of the basal reflection was determined by curve fitting a Gaussian-Lorentzian lineshape to the diffraction pattern after baseline correction using GRAMS/32 software, version 5.2 (Thermo Electron Corporation, Waltham, MA).

RESULTS AND DISCUSSION

Sample Characteristics and Influence of Mineralogy on Water Adsorption

The clay fraction of the Blount soil was comprised of illite, hydroxy-interlayered vermiculite, kaolinite, and quartz (Table 1) (Dontsova and Norton, 2002). The Fayette clay was dominated by randomly interstratified illite-smectite (I/S), but also contained kaolinite, illite, vermiculite, and quartz. Swelling material in both soils was randomly interstratified with illite, which resulted in broad, ill-defined peaks, and d-spacings lower than generally expected for pure materials (Laird et al., 1991). The difference in mineralogical composition of the clays was reflected in a larger EGME surface area for the more expandable Fayette sample as compared with the illitic Blount clay.

The most prominent feature of the FTIR spectra from both clays was a wide band at 1060 cm^{-1}, which corresponds to the Si–O stretch of the phyllosilicate clay structure (Farmer, 1974) (Fig. 1). This band was not fully resolved because of the considerable thickness of the clay film. Other structural vibrations were also observed. Bands at 3630 and 3697 cm^{-1} corresponded to stretching vibrations of structural OH groups. The 3697 cm^{-1} band is characteristic of kaolinite and the 3630 cm^{-1} band is commonly found in many different phyllosilicate minerals (Johnston and Aochi, 1996). The 693 cm^{-1} band is a structural OH libration, and a band at 913 cm^{-1} corresponds to a deformation mode of the Al$_2$OH group. There was also some quartz present as indicated by bands at 799 and 780 cm^{-1}.

Organic matter in the clays (Table 1) was responsible for bands at 2923 and 2852 cm^{-1} (aliphatic C–H stretching mode), and the 1420 cm^{-1} band was attributed to the presence of carbonate (Johnston and Aochi, 1996). The remaining bands were assigned to water vibrations. Bands at 3580 and 3420 cm^{-1} are stretching vibrations (ν_3 and ν_1 modes), whereas the 1635 cm^{-1} band is the H–O–H bending band of water (ν_2 mode) with an overtone occurring at 3250 cm^{-1} (Pimentel and McClellan,
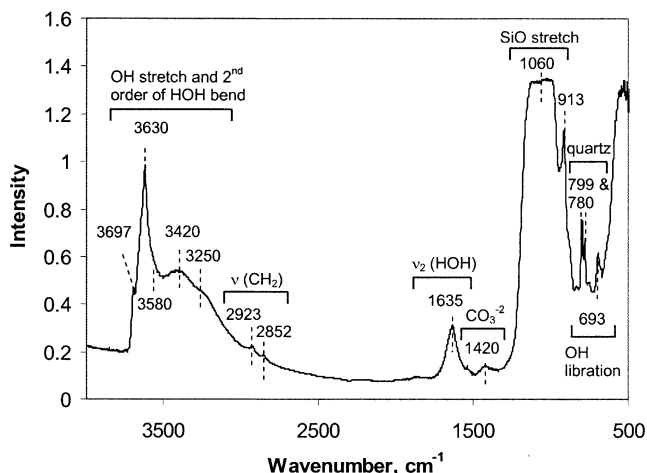

Fig. 1. Sample Fourier transform infrared (FTIR) spectrum of the Ca-exchanged Fayette sample at 0.02 P/P$_0$.

1960; Johnston et al., 1992; Venyaminov and Prendergast, 1997; Xu et al., 2000).

The stretching vibrations of water overlap with each other and with the structural OH vibrations at 3630 cm^{-1} (Fig. 1), making an exact determination of their position and absorbance values difficult (Johnston et al., 1992). In contrast, the H–O–H bending band of water at 1635 cm^{-1} is not subject to these interferences, and it was used in further analyses of sorbed water. Infrared spectra obtained from the self-supporting films showed an increase in the intensity of the H–O–H bending band of water at 1640 cm^{-1} with an increase in the partial pressure of water vapor (Fig. 2). The increase in intensity of the 1640 cm^{-1} band obeyed the Beer-Lambert law, which states that absorbance, $A(\nu)$, is linearly related to the concentration of the absorber, c, and thickness of the film, d, with molar absorptivity, also called the extinction coefficient, $\varepsilon(\nu)$, being specific to the absorber (Atkins, 1998, p. 458)

$$A(\nu) = \varepsilon(\nu)cd \qquad [3]$$

At $P/P_0 < 0.45$, a linear relationship was observed between the absorbance of the 1640 cm^{-1} band and sample weight. The intercept of the regression line at zero absorbance was considered the dry weight of the sample as recommended by Johnston et al. (1992) and Xu et al. (2000). Change in the molar absorptivity of water with clay dehydration has been reported by several researchers (Poinsignon et al., 1978; Johnston et al., 1992; Xu et al., 2000). Problems due to changes in $\varepsilon(\nu)$ were avoided in this study by using only the linear portion of the plot at <0.45 P/P_0.

Sorption isotherms were Type II (S-shaped), as commonly found for the sorption of water by clay (Fig. 2a) (Newman, 1987). The expandable (I/S) Fayette clay sorbed more water than the clay fraction from the Blount soil, which was composed primarily of illite and vermiculite. The effect of other minerals present in the samples was considered to be minor because of their smaller specific surface areas (Laird, 1999). A hysteresis effect was observed between the adsorption and desorption legs of the isotherms for both soil clays (Fig. 3), but the expandable (I/S) Fayette clay exhibited a greater hysteresis than the illitic Blount clay. For the Fayette clay, hysteresis was similar to that reported for specimen smectites (Mooney et al., 1952a; Keren and Shainberg,
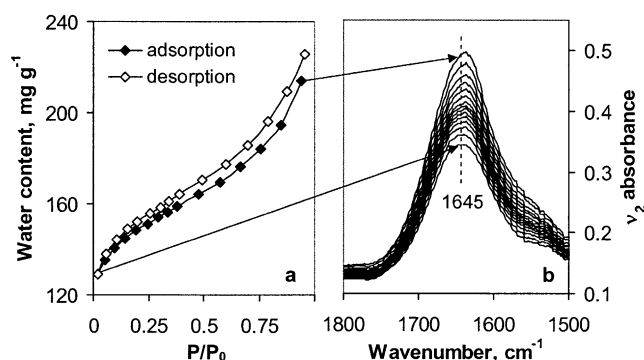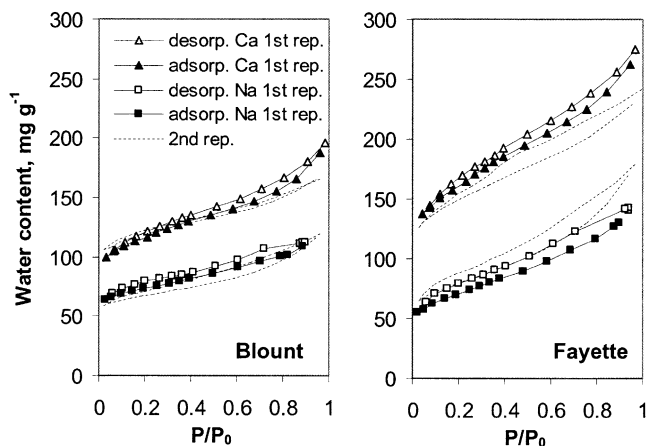

Fig. 3. Variability between replicates (solid vs. dashed lines) and hysteresis associated with adsorption (solid markers) and desorption (empty markers) legs of the isotherm for Fayette and Blount samples exchanged with Ca (triangles) and Na (squares).

1975; Berend et al., 1995; Cases et al., 1997; Xu et al., 2000). According to Keren and Shainberg (1975), the hysteresis behavior of smectite may arise from one or more of the following factors: (a) capillary condensation, (b) a change in rigidity of the water adsorbed on exchangeable cations between the clay platelets, and (c) a variety of geometric situations in which the filling and emptying pathways are different. The capillary and geometric factors are more pronounced in desorption curves.

Some variability was observed between the replicates (Fig. 3), and the variability was greater in the Fayette clay compared with the Blount clay resulting in fewer significant differences between treatments (Table 2). Some researchers working with specimen clay minerals (Mooney et al., 1952a) have observed that desorption isotherms are more reproducible because of differences in the initial water content of the samples resulting from the drying method, for example, evacuation vs. high temperature. In this study, both desorption and adsorption isotherms were reproducible, and adsorption legs were used for further analyses because they were less affected by capillary condensation of water and were more directly related to the interaction between adsorbed water, exchangeable cations, and the clay surfaces (Keren and Shainberg, 1975, 1979).

Table 2. Water content and water bending band position for Mg^{2+}, 50:50 Ca^{2+}/Mg^{2+}, Ca^{2+}, Na$^+$, and K$^+$ exchanged soil clays averaged across all P/P_0.

Treatment	Water content		Band position	
	Blount	Fayette	Blount	Fayette
	mg g^{-1}		cm^{-1}	
Mg^{2+}	160 A b†	227 A a	1643.5 A a	1644.6 A a
50:50 Ca^{2+}/Mg^{2+}	136 B b	200 AB a	1641.1 AB a	1642.5 B a
Ca^{2+}	130 B b	178 B a	1639.7 B a	1640.9 C a
Na$^+$	80 C a	92 C a	1639.4 B a	1639.7 CD a
K$^+$	59 D a	91 C a	1639.8 B a	1639.3 D a
LSD	7	46	3.1	1.6

† Numbers followed by the same letter within a column are not significantly different at the 95% level by t test. Capital letters are for comparison between cation treatments within a clay; lower case letters are for comparison across clays.
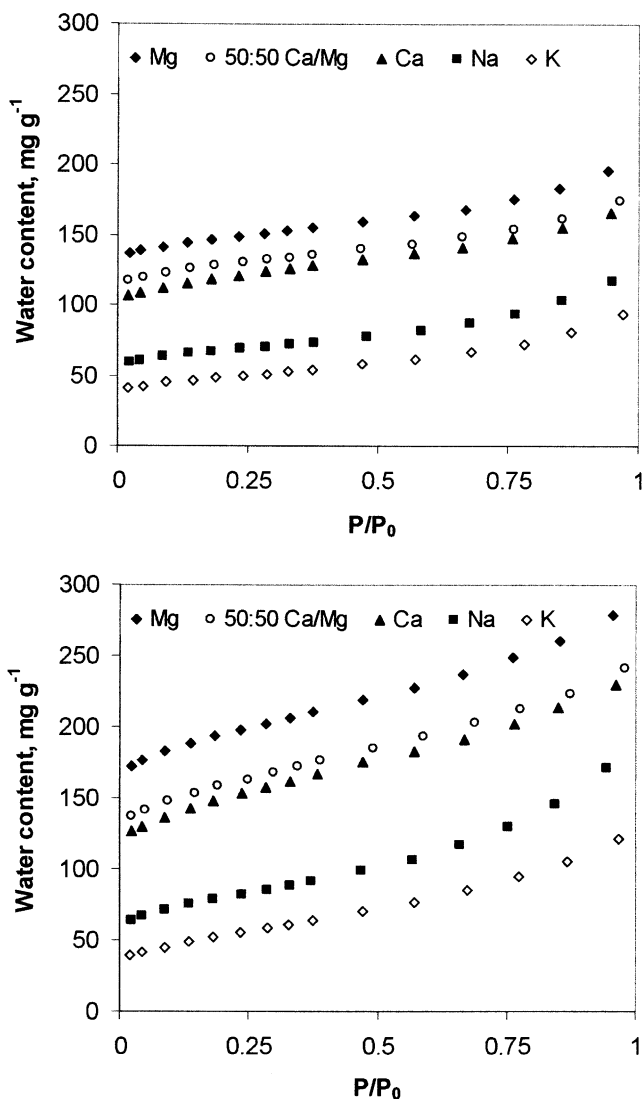

Fig. 2. (a) Adsorption and desorption isotherms and (b) FTIR spectra in the ν_2(HOH) region for a Mg-exchanged Blount sample.

Fig. 4. Water adsorption isotherms for Ca^{2+}, 50:50 Ca^{2+}/Mg^{2+}, Mg^{2+}, K^+, and Na^+ exchanged Blount and Fayette soil clays.

The Influence of Exchangeable Cations on Water Adsorption

The amount of adsorbed water was influenced by the exchangeable cation with the order of increase being: $K^+ < Na^+ < Ca^{2+} < 50:50\ Mg^{2+}/Ca^{2+} < Mg^{2+}$ (Fig. 4).

Clays exchanged with monovalent cations sorbed less water than clays exchanged with divalent cations. Smaller, more hydrated, cations (Na^+ and Mg^{2+}) also increased water sorption compared with larger cations (K^+ and Ca^{2+}).

Statistical analysis of the data showed that exchangeable cations, as a treatment, had a highly significant effect on the amount of water adsorbed by both soil clays ($P > F = 0.0001$ for Blount and $P > F = 0.0032$ for Fayette). The water content averaged across all values of P/P_0 was significantly greater with Mg than with Ca (Table 2). The amount of water sorbed by samples exchanged with the 50:50 mixture of Ca and Mg was in between the values for pure Ca and Mg samples in agreement with previous studies of mixed Ca/Na smectite by Keren and Shainberg (1979) and Na/Mg bentonite by Madejova et al. (2002). In both soil clays, the amount of water adsorbed by samples exchanged with monovalent cations was significantly less than when exchanged with divalent cations. In the Blount clay, the differences between Na- and K-samples were also statistically significant at the 5% level. In the Fayette clay, differences in water sorption by clays exchanged with monovalent cations were not statistically significant. The differences between the amount of water sorbed by Blount and Fayette clays were significant only for Ca, Mg, and the mixture of Ca and Mg, with Fayette adsorbing more water.

To compare values obtained in this study to published data, interpolated water contents at a P/P_0 of 0.5 were also calculated (Table 3). The amount of water sorbed by Fayette clay (dominated by I/S) compares well with published data for specimen smectites. The reported range of water sorption by smectites exchanged with Ca is 125 to 265 mg g^{-1}, averaging 191 mg g^{-1} (Table 3). The 186 mg g^{-1} measured for the Ca-Fayette sample in this study falls within this range. The wide range of values reported for water sorption by smectites has been explained by: (i) preparation of the sample, including the size fraction used; (ii) the reference weight of dry clay; (iii) hysteresis in the adsorption–desorption cycle; and (iv) surface contaminants (Newman, 1987). In this study, the presence of other phyllosilicate minerals and quartz, Fe and Al oxides, and OM likely influenced the total amount of adsorbed water. Despite some variation

Table 3. Reported values for water sorption by clay minerals at $P/P_0 = 0.5$.

| Clay mineral	Conditions of acquisition	Amount of adsorbed water				Reference
		K^+	Na^+	Ca^{2+}	Mg^{2+}	
		mg g^{-1}				
Wyoming bentonite	desorption	95	140	220	195	Mooney et al. (1952b)
Wyoming bentonite	adsorption	–	80	200	–	Keren and Shainberg (1975)
SWy montmorillonite	desorption	50	88	155	–	Hall and Astill (1989)
Wyoming montmorillonite	adsorption	49	72	166	126–198	Berend et al. (1995) and Cases et al. (1997)
SWy-1 montmorillonite	desorption	43	63	176	–	Chiou and Rutherford (1997)
SWy-1 montmorillonite	adsorption	–	60	125	125	Dios Cancela et al. (1997)
SWy-1 montmorillonite	adsorption	–	95	–	–	Xu et al. (2000)
SAz-1 montmorillonite	desorption	82	138	223	–	Chiou and Rutherford (1997)
SAz-1 montmorillonite	adsorption	–	140	265	370	Xu et al. (2000)
Average		64	97	191	203	
Fayette soil clay	adsorption	73	96	186	234	Current study
Blount soil clay	adsorption	61	81	134	163	Current study
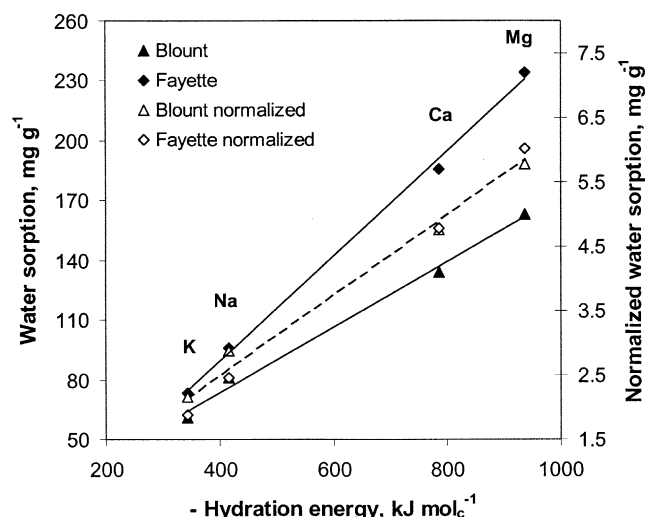
Fig. 5. Average values, unnormalized (left axis) and normalized by the clay cation exchange capacity (right axis), for the amount of water adsorbed by Blount and Fayette soil clays at P/P_0 0.5 as a function of hydration energy of the exchangeable cations per mole of charge (Table 4). Solid lines correspond to linear regressions for Blount ($y = 0.1647x + 7.2470$, $R^2 = 0.99$) and Fayette clay ($y = 0.2636x - 16.2440$, $R^2 = 0.98$) using unnormalized data; the dashed line corresponds to the combined regression for both soil clays using normalized data ($y = 0.0063x - 0.0316$, $R^2 = 0.98$).

in published results, our data agree with other studies regarding the relative effect of exchangeable cations on water sorption by specimen clays.

For the four cations included in this study, correlations of hydration energy per mole of charge with the amount of water adsorbed on the samples at a P/P_0 of 0.5 (Fig. 5) resulted in a highly significant linear relationship ($P > F < 0.0001$). The amount of water sorbed increased as the hydration energy of the exchangeable cation increased. The amount of water sorbed was also influenced by the properties of the clay material. Slopes of the regression between amount of adsorbed water and hydration energy of the exchangeable cations for the two clays were significantly different ($P > F < 0.0001$). The Fayette clay had 1.6 times greater slope than the Blount clay; however, if amount of adsorbed water was divided by cation exchange capacity (CEC), slopes for the two soil clays became the same ($P > F = 0.9424$). These results indicate that hydration of exchangeable cations is the primary driving force for water sorption by the two clays and confirm that water, as a polar molecule, has a greater affinity for cations adsorbed on the clays than for the siloxane surface of the 2:1 clays themselves (Chiou and Rutherford, 1997). Similar effects of clay CEC on water sorption can be derived from data reported by Xu et al. (2000). Decrease in effective hydration numbers with increase in CEC (Laird, 1999)

Table 5. Brunauer–Emmett–Teller (BET) parameters, monolayer coverage (x_m) and surface area (S_m), for Mg^{2+}, 50:50 Ca^{2+}/Mg^{2+}, Mg^{2+}, Na^+, and K^+ exchanged Blount and Fayette clays.

Treatment	Blount		Fayette	
	x_m	S_m	x_m	S_m
	mg g^{-1}	m^2 g^{-1}	mg g^{-1}	m^2 g^{-1}
Mg^{2+}	104 a†	368 a	145 a	514 a
50:50 Ca^{2+}/Mg^{2+}	88 b	313 b	124 a b	440 a b
Ca^{2+}	85 b	302 b	114 b	403 b
Na^+	51 c	179 c	57 c	201 c
K^+	37 d	130 d	46 c	162 c
LSD	6	24	30	106

† Numbers followed by the same letter within a sample are not significantly different at the 95% level by t test.

was not observed in this study. Organic matter and sesquioxides restrict both the collapse of expandable clay interlayers on dehydration and their swelling on hydration, they may also effectively block some interlayer spaces. This, as well as water adsorption by OM itself, may result in diminishing effects of clay structure and apparent increases in the exchangeable cation effect.

A highly significant but weaker linear relationship also existed between the amount of adsorbed water and the ionic potential of the cations (Table 4) ($P > F < 0.0001$). This result can be explained by a correlation between hydration energy per mole of charge and ionic potential of the cations ($P > F < 0.0209$). A similar relationship was observed by Dios Cancela et al. (1997), who showed that the total heat of adsorption of H_2O sorbed by smectite was positively correlated with the ionic potential of the exchangeable cations and concluded that water molecule-cation interactions were electrostatic in nature.

According to Keren and Shainberg (1979), the adsorption of water on clays usually involves the formation of multilayers, so the adsorption isotherm can be analyzed according to BET theory. While there are theoretical limitations to the BET equation application to water sorption by soils and clays, for example, strong effect of cations and restricted interlayer adsorption, BET equation is useful for comparison with published results. When the BET equation was applied to these data, a linear relationship between P/P_0 and $P/P_0/q(1 - P/P_0)$ was obtained over the P/P_0 range of 0 to 0.35. Monolayer coverage and surface area of the clays exchanged with different cations were calculated (Table 5) and the relative magnitudes were in agreement with surface areas measured by the EGME method (156 m^2 g^{-1} for Blount and 255 m^2 g^{-1} for Fayette; Table 1). For each clay sample, surface area increased with hydration of the cation, confirming that water sorption was driven largely by hydration of the exchangeable cations, as reported previously for bentonite by Mooney et al. (1952a). Mono-

Table 4. Selected properties of K^+, Na^+, Ca^{2+}, and Mg^{2+}.

Property	K^+	Na^+	Ca^{2+}	Mg^{2+}	Reference
Ionic radius, Å	1.33	0.95	0.99	0.65	Burgess (1988, p. 55)
Ionic potential†	0.75	1.05	2.02	3.08	
Gibbs free energy of hydration, kJ mol^{-1}	−345	−417	−1570	−1875	Burgess (1988, p. 54, 58)
Hydration number	4.7	5.0	10.4	18.1	Ohtaki and Radnai (1993)

†Ratio of valence to ionic radius.

layer coverage also increased with an increase in the CEC of the clay. Values for the Fayette clay (57 mg g^{-1} for Na-exchanged clay and 114 mg g^{-1} for Ca-exchanged clay) were in excellent agreement with those reported for Na and Ca smectites by Keren and Shainberg (1975) (58 and 114 mg g^{-1}, respectively) and by Dios Cancela et al. (1997) (11–52 and 103 mg g^{-1}, respectively). Generally, much better agreement was found between this study and published reports, as well as among published reports (Keren and Shainberg, 1975; Dios Cancela et al., 1997) if the amount of water for monolayer coverage was compared rather than sorption at 0.5 P/P$_0$.

Character of Water Adsorbed by Soil Clays

As noted previously, the position and intensity of the IR deformation band of water at 1640 cm^{-1} can be used to evaluate the water environment on clay surfaces (Russell and Farmer, 1964; Poinsignon et al., 1978; Johnston et al., 1992; Xu et al., 2000; Madejova et al., 2002). In this study, it was found that exchangeable cations had a highly significant effect on the average position of the water deformation band for the Fayette clay ($P > F = 0.0029$), and significant at the 10% level for the Blount clay ($P > F = 0.0799$) (Table 2). The presented data were collected during adsorption; however, the position of the ν_2 band exhibited little hysteresis. In both clays the position of the band shifted to greater frequencies for cations with greater ionic potential indicating stronger H bonding. In agreement with Madejova et al. (2002), the average frequency of the water bending vibration decreased in the following order: $Mg^{2+} > 50:50$ $Ca^{2+}/Mg^{2+} > Ca^{2+} > Na^+ > K^+$. These results also support calculations made by Poinsignon et al. (1978) from spectroscopic data, which indicate that the more polarizing a cation, the higher the polarity of associated water molecules. In the Blount clay, the ν_2 frequency for the K-exchanged sample did not follow the established order and only Mg was significantly different from the other cations. Fayette samples were significantly different from each other except for those exchanged with K and Na. The position of the water deformation band for the same cation across the soil clays was slightly less for the Blount clay, with the exception of the K treatment, but these differences were not statistically significant.

In addition to the difference in the average position of the ν_2 mode of water for clays exchanged with different cations, the spectra showed a shift in the position of the water-bending band with a change in RH (Fig. 6). According to Pimentel and McClellan (1960), the frequency of the bending mode of water shifts to larger wavenumbers as the extent of H bonding increases. The position of the water deformation band changed to greater frequencies for both Ca-clays with an increase in P/P$_0$, indicating more H bonding. By contrast, in the Mg-treatment, the band shifted to lesser numbers meaning less H bonding. Clay samples exchanged with a mixture of Ca and Mg showed an intermediate behavior.

At high RH, as the effect of cations on water was decreasing, water deformation band frequencies of the

Ca- and Mg-samples tended to converge (Fig. 6). The position of the H–O–H bending band at high P/P$_0$ was about 1642 cm^{-1} for the Blount clay and about 1643.5 cm^{-1} for the Fayette clay. These concur with literature values for bulk water (Venyaminov and Prendergast, 1997). Even at high water contents, when little cation effect was expected, observed ν_2 frequencies were somewhat different between cations. The fact that greater differences in the position of the water deformation band between treatments were observed at low water contents is consistent with the observations of Sposito and Prost (1982), who concluded from several studies that clay surface and cation influence extend for only a few layers of water, and the rest of the water behaves like bulk water. Infrared spectroscopy samples all the water molecules present in the sample (Xu et al., 2000), and averages values for perturbed water molecules around the cations and relatively unaffected water on clay surfaces and in pores.

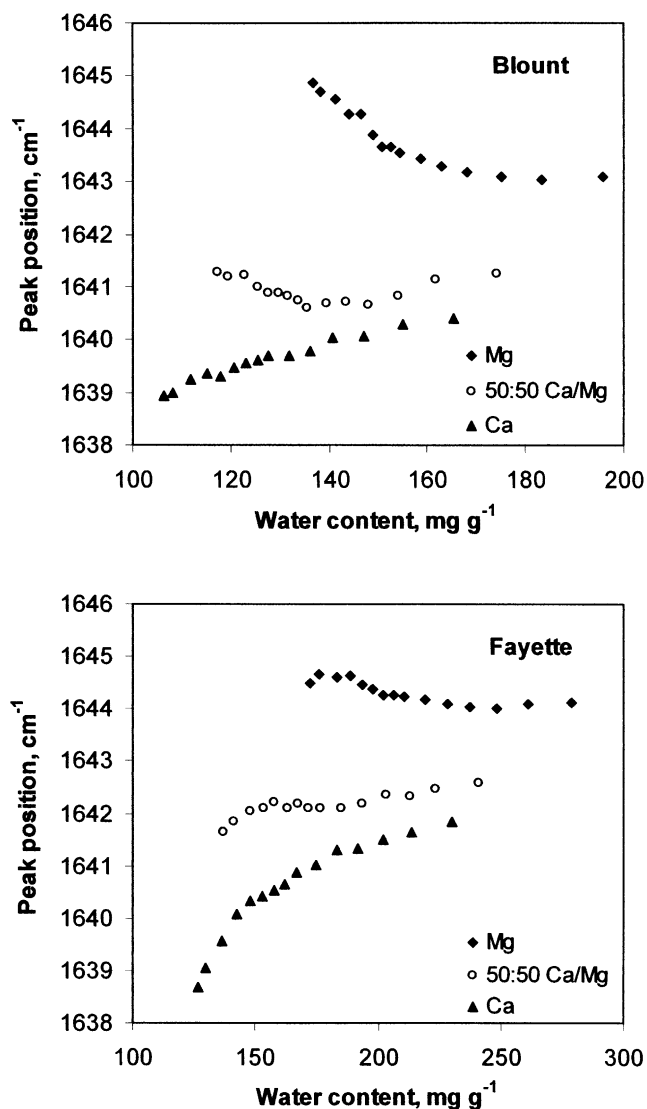Similar to the Ca-exchanged soil clays in this study,

Fig. 6. Water deformation band position for Ca^{2+}, Mg^{2+}, and 50:50 Ca/Mg treatments.

Yan et al. (1996) observed a decrease in the position of the v_2 mode of water at low water contents. They explained the decrease by an effect of electric fields associated with discrete surface charges on the clay, which strongly orient water molecules. A resultant loss of freedom by water molecules restricts their ability to form H bonds. Contrary to Yan et al. (1996), who concluded that structural modification reflected by v_2 is essentially independent of the cationic species, Poinsignon et al. (1978) and Johnston et al. (1992) assigned the change in v_2 frequency to the polarizing effect of exchangeable cations on the clay, which attract and orient water molecules. The strong cation effect on the water deformation band observed in this study supports the latter theory.

Clay Swelling as Affected by Exchangeable Calcium and Magnesium, and Partial Pressure of Water Vapor

When the soil clays were exposed to N_2 gas at different RHs, swelling was observed by x-ray diffraction with an increase in P/P_0 of water (Fig. 7 and 8). Expandable components of both clays formed the equivalent of one-layer hydrates with a d-spacing of about 1.2 to 1.3 nm at low RH (Fig. 8). The presence of interlayer contaminants, such as OM and hydroxy-Al polymers, may have prevented total collapse of the structure and thereby allowed interlayer water to be retained even in a dry environment. At high RH, the expandable component in the Blount clay expanded to 1.4 nm or the equivalent of a two-layer hydrate, whereas the Fayette soil clay expanded to 1.7 nm, corresponding to three layers of interlayer water.

Expansion was fairly gradual, unlike some previous studies of specimen smectite (Mooney et al., 1952b; Keren and Shainberg, 1975; Dios Cancela et al., 1997) where step-wise swelling corresponding to an integral number of water layers was reported. Step-wise swelling

suggests the initial formation of a hydration shell around the cation, followed by a filling of the remaining interlamellar space (Cases et al., 1997). Gradual increase in d-spacing with water adsorption on smectites (Johnston et al., 1992; Berend et al., 1995; Dios Cancela et al., 1997) could indicate either an interstratification of one or two layers of water molecules (Berend et al., 1995; Cases et al., 1997) or a change in the position of adsorbed molecules during the hydration process (Dios Cancela et al., 1997).

If interstratification contributed to the observed swelling patterns, it may be that slightly smaller d-spacings than expected for integral numbers of water layers in the Blount clay (1.2 vs. 1.25 nm at low RH and 1.4 vs. 1.5 nm at high RH) can be explained by a fraction of the interlayers (about 1/5) not expanding at all. This would be consistent with the mineralogy of the clay, dominated by illite and vermiculite but including randomly interstratified layers of low and high charge. Random interstratification of illite and smectite would also explain the broad character of the low-angle peak of the Fayette clay and its incomplete expansion to 1.8 nm (Laird et al., 1991).

Cases et al. (1997) observed that the relative pressure corresponding to the formation of a two-layer hydrate in montmorillonite decreased with increasing hydration energy of the interlayer cation, with Ca samples forming a complete two-layer hydrate at a P/P_0 of 0.7, whereas Mg samples did so at $P/P_0 = 0.4$. Similar trends were also reported for Sr^{2+} and Ba^{2+}. Their results also showed that during desorption, Mg-smectite and Ca-smectite retained two layers of water until a P/P_0 of 0.2 and 0.65, respectively. Such differences were not observed in this study. The Ca-Fayette clay swelled to the equivalent of a full two-layer hydrate at a P/P_0 of 0.4, with its water content corresponding to only 1.45 monolayers of water. This was a slightly lower P/P_0 than in the Mg-Fayette sample. The Fayette clay at high RH adsorbed enough water for two complete monolayers, but the d-spacing corresponded to more than two layers of water, indicating that the formation of a third layer
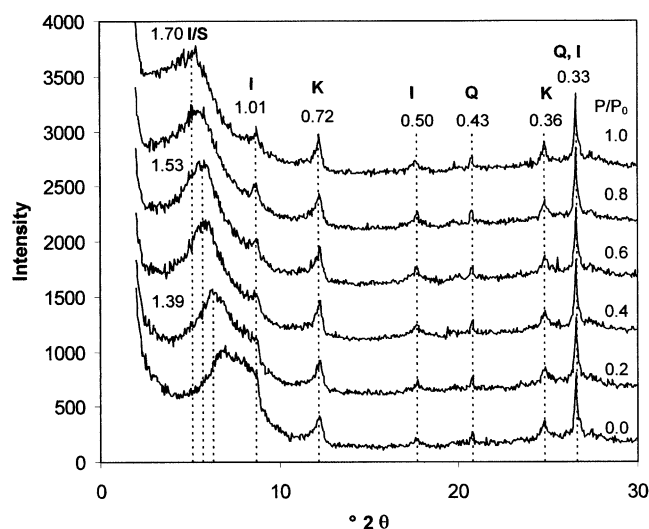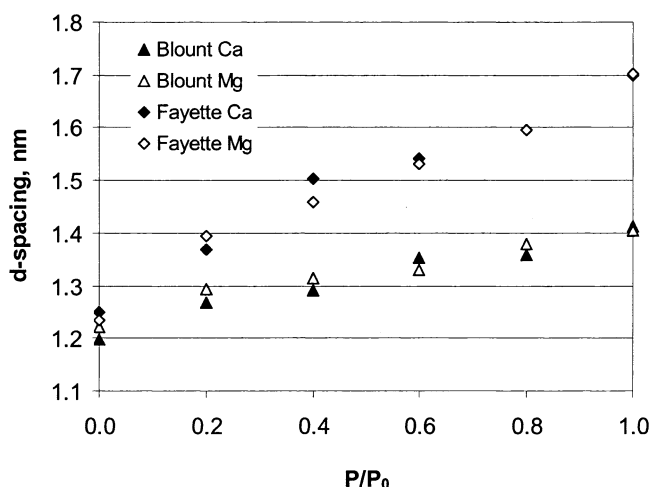

Fig. 7. X-ray diffraction patterns of Ca-exchanged Fayette clay with an increase in partial pressure of water vapor. Clay minerals identified: I—illite, I/S—randomly interstratified illite/smectite, K—kaolinite, and Q—quartz. Peak positions are in nanometers (nm).

Fig. 8. Measured d-spacings of expandable soil clay components as a function of P/P_0. Each point corresponds to one x-ray diffraction pattern.

started before the formation of the second layer was complete. The ability of the Fayette clay to form a third layer of water can be attributed to the lower charge density of the smectite component as compared with illite and vermiculite. Blount clay at high P/P_0 had a basal spacing of 1.4 nm and approximately two monolayers of water in both Ca and Mg samples; however, for Mg samples the amount of water required to form a monolayer was greater than for Ca.

No differences in the d-spacing of oriented mounts of Ca- and Mg-exchanged soil clays at different RHs were observed. This generally agrees with most available reports (MacEwan and Wilson, 1980), which show little or no difference in the expansion of specimen Ca- and Mg-clays in water vapor. An explanation may be that the excess water in the Mg-clays is adsorbed on the surface of tactoids. According to Laird (1999), surface sorption is an important mechanism of water sorption by clays, and between P/P_0 of 0.4 and 0.8, it predominates over filling of the interlayers and swelling. Laird (1999) also observed that the volume of water sorbed on the surface of clay particles was greater than the volume of the interlayer region, because charge sites on external surfaces have substantially greater effective hydration numbers than charge sites on internal surfaces. This explanation is consistent with the fact that the hydration of cations (and the associated charge sites) on external surfaces is unconstrained, whereas the hydration of cations/charge sites on internal surfaces is limited due to the available interlayer volume per unit charge. Magnesium-clays, which are prone to dispersion, likely formed smaller tactoids and therefore had greater external surface area with unconstrained sorption potential. On the other hand, increased water sorption on particle surfaces of Mg-clays and stronger H bonding of this water can indicate a greater potential for clay dispersion, as these external surfaces of clay particles are responsible for flocculation.

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